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GCA Corp, Bedford, Mass GCA Technology Div

Prepared for

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Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
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ASSESSMENT OF ACRYLONITRILE AS A POTENTIAL AIR POLLUTION PROBLEM

Volume VI

by

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Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION 1

SUMMARY AND CONCLUSIONS

Acrylonitrile is a colorless, highly flammable liquid with a characteristic unpleasant, irritating odor. Manufacture in the U.S. is based on a reaction between propylene, ammonia, and air; and its primary use is in the production of acrylic and modacrylic fibers such as Acrilan, Orlon, and Courtelle.

Acrylonitrile is toxic when inhaled, ingested, or absorbed through intact skin. It is a severe skin and eye irritant. Its high toxicity is due to the liberation of free cyanide in the body, which inhibits enzymes responsible for cellular respiration. The occupational standard for an 8-hour time weighted average is 20 ppm, based on animal studies and human data on hydrogen cyanide exposure.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at less than 5 ppm. The maximum 24-hour average ambient concentration might be expected to be less than 3 ppm.

About 1.4 billion pounds of acrylonitrile were produced at five plants in 1974, with almost 60 percent of this being used in the manufacture of acrylic fibers. Production is expected to increase at 9.9 percent per year through 1978. The primary emission sources in descending order are production, end product manufacture, and bulk storage. Total emissions are estimated to have been about 31 million pounds in 1974.

Emissions from manufacture occur mainly from the main process absorber vent, which is uncontrolled at most U.S. plants. Four control devices are,

however, available: CO-boiler, thermal incinerator, incinerator plus steam generation, and a flare system. The most feasible method of reducing emissions from existing plants is thermal incineration. Fixed-roof storage tanks can be controlled by venting to one of these devices, or they can be converted to floating roof design.

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, it appears that acrylonitrile as an air pollutant does not pose a threat to the health of the general population. In addition, acrylonitrile does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time. However, the acrylonitrile industry is projected to grow and problems could arise near emission sources. While the maximum expected ambient concentration estimates are admittedly quite conservative, these concentrations are a significant fraction of the occupational standard, especially when the possibility of continuous exposure is considered. It is suggested that acrylonitrile be reassessed periodically to ensure that a problem does not accompany its increased use.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Acrylonitrile is a colorless liquid with a characteristic unpleasant, irritating odor. Most acrylonitrile is manufactured based on the reaction between propylene, ammonia, and air. It is used primarily as a monomer or copolymer for the production of acrylic and modacrylic fibers such as Acrilan, Orlon, and Courtelle. It is also used for making nitrile rubbers, in surface coatings, and as a copolymer with butadiene and styrene in the manufacture of ABS plastics and resins. Significant properties of acrylonitrile are listed in Table 1.

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Acrylonitrile is an acute poison as well as a severe skin and eye irritant.[1] It is toxic when inhaled, ingested, or absorbed through intact skin. Dose-response data for humans have not been documented in the literature. Clinical exposure data that do exist note several cases of mild jaundice in workmen handling acrylonitrile.[2] Other symptoms of exposure included nasal and respiratory oppression, vomiting, nausea, weakness, fatigue, headache, and diarrhea. One fatal case involved a child who slept in a room fumigated with acrylonitrile, while adults in the room experienced no discomfort. At death there was pink discoloration of the face, extensive lividity, hyperemia, and congestion of all viscera.[2] Death was due to respiratory collapse.

Table 1. SIGNIFICANT PROPERTIES OF ACRYLONITRILE

Synonyms	Propenenitrile, vinyl cyanide, cyanoethylene
Chemical formula	$CH_2 = CHCN$
Molecular weight	53.06
Boiling point	77.3°C
Melting point	-83°C
Specific gravity	0.8004 (25°/4°C)
Vapor density	1.9 (air = 1)
Vapor pressure	83 mm Hg at 20°C, 110-115 mm Hg at 25°C
Solubility	7.3% by weight in water at 25°C. Soluble in all common organic solvents.
Explosive limits	3.0 to 17.0% by volume in air at 25°C
Ignition temperature	481°C
Flash point	-1°C (closed cup)
At 25°C and 760 mm Hg	1 ppm vapor = 2.17 mg/m^3 1 mg/m^3 = 0.461 ppm

Acrylonitrile's high degree of toxicity is due to the liberation of free cyanide in the body. Cyanide easily diffuses to all body tissues and rapidly inhibits specific enzymes responsible for respiration on the cellular level, stopping the utilization of molecular oxygen by cells. The symptoms of acrylonitrile poisoning are typical of hydrogen cyanide poisoning, but with the onset of symptoms slightly delayed. Higher concentrations of acrylonitrile are needed to produce the same toxic effects as lower concentrations of hydrogen cyanide. A concentration of 270 ppm hydrogen cyanide is immediately fatal to man, while 18-36 ppm may produce slight symptoms after several hours.[1] The U.S. Occupational Standard for an 8-hour time weighted average exposure for acrylonitrile is 20 ppm,[3] based on animal response data and comparisons made to human data available on exposure to hydrogen cyanide.[4] A concentration of 20 ppm represents less than one-half the concentration that produced toxic effects in dogs after 4 hours, the most susceptible animal studied.

Acrylonitrile odor can be detected in air without any background interferences at 21.4 ppm.[5] However, human response to its odor rapidly fatigues and is unreliable as a warning.

Chronic Poisoning - Ill effects due to chronic exposure to acrylonitrile have not been documented in man. However, based on animal inhalation studies, there is no evidence for the cumulative action of acrylonitrile.[6]

Effects on Animals

Acute Poisoning - The effects of single exposures to acrylonitrile are summarized in Table 2[7,8] and Table 3.[8] All animals displayed the same series of symptoms, but at different concentrations. There was an initial stimulation of respiration followed by rapid, shallow breathing. Breathing then became slow, with gasping and spasm-like convulsive movements of the abdominal wall. Coma preceded respiratory failure. After death the skin appeared darkened with the blood very dark red. The mechanism of death, as in man, was due to respiratory inhibition by the cyanide ion except in guinea pigs, where death was caused by pulmonary edema. Susceptibility varied considerably. In rats, 300 ppm produced only slight mucous membrane irritation followed by a reddening of the skin, nose, ears, and feet. At 100 ppm dogs were rendered comatose and convulsive.[8]

A single nonlethal exposure to acrylonitrile produced no lasting effects in all animals except dogs and guinea pigs. Guinea pigs died up to 5 days after exposure as a result of pulmonary edema, while dogs showed toxic effects up to 10 days following exposure due to severe anoxemia, or a deficiency of oxygen in the blood. In another study,[9] histologic changes characteristic of anoxia were found in the brains of rats exposed for 7 hours to 100 or 75 ppm; of dogs exposed to 100, 75, or 50 ppm; and of rhesus monkeys exposed to 75 ppm.

Table 2. ACUTE RESPONSE OF ANIMALS TO ACRYLONITRILE[7,8]

Animal	Concentration, ppm	Time, hr	Response
Mice	690	0.5	5/6 died within 24 hours
	276	0.5	No fatalities
Rats	1270	0.5	Marked. No effects in 24 hours
	665	0.5	Moderate, transitory
	1490	1.0	25% dead 4 hours after exposure
	1270	1.0	Marked. Recovery in 48 hours
	665	1.0	Marked, transitory
	1260	2.0	Fatal. 100% dead 4 hours after exposure
	595	2.0	Marked, transitory

Table 3. ANIMAL RESPONSES TO SINGLE 4-HOUR EXPOSURES TO ACRYLONITRILE[8]

Animal	Weight, gm	Concentration, ppm	Response
Rats	295	685	Fatal up to 2 to 6 hours after test.
		315	Some deaths. Survivors recover in 24 hours. Slight transitory effects.
		100	Slight transitory effects.
Guinea pigs	695	575	Eye and nose irritation during test. Delayed deaths in 3 to 6 days from lung edema.
		100	Slight to no effects.
Rabbits	4,530	260	Fatal up to 4 to 5 hours after test.
		135	Marked effects; transitory.
Cats	3,620	900	Death in convulsions, 1-1/2 hours after test.
		275	Salivation, bowling, pain. Marked effects. Recovery in 24 hours.
		100	Salivation. Slight transitory effects.
Dogs	5,500	165	Convulsions in 2 hours. Dead 3 hours after exposure.
	11,400	165	In coma at end of exposure. Dead within 40 hours.
	12,000	100	Severe salivation during test. Recovery in 24 hours.
	5,900	100	Convulsions in 2-1/2 hours. In coma at end of test. Partial paralysis of hind legs for 3 days.
	5,000	65	In coma. Died in 8 hours.
	5,700	30	Slight salivation. No other effects.
Rhesus monkeys	4,200	90	Slight redness of face, genitals, weakness. Normal in 12 hours.
	4,800	65	Slight stimulation of respiration.

Orally the LD_{50} in the mouse is on the order of 35 mg/kg, in the rat 78 mg/kg, and in the guinea pig, about 90 mg/kg body weight.[1] For skin absorption in rabbits, the LD_{50} is 280 mg/kg.[3] A dose of 0.05 ml of acrylonitrile dropped into the eyes of rabbits produced irritation and an immediate closing of the eye and shaking of the head. After 24 hours, there was no sign of any eye irritation.[7]

Chronic Poisoning - Table 4[6] summarizes animal response to chronic exposure to acrylonitrile. The authors concluded that no evidence of cumulative action was observed in any animal which survived. Rats, guinea pigs, rabbits, monkeys, and cats exposed to 153 ppm, 4 hours/day for 5 days/week for 8 weeks showed varying degrees of eye and nose irritation, loss of appetite, gastro-intestinal disturbances, and hind leg paralysis from which recovery was often rapid. Chronic exposure to 56 ppm had a toxic effect on dogs. One dog died in convulsions, while the other developed a transitory weakness simulating paralysis of the hind legs.

Table 4. ANIMAL RESPONSE TO CHRONIC EXPOSURE TO ACRYLONITRILE,[6] 4 HOURS/DAY FOR 5 DAYS/WEEK

Animal	Number	Concentration, ppm	Response
Rhesus monkeys	2	153	Sleepiness, weakness, vomiting, salivation. One died in 6 weeks.
	4	56	No toxic effects.
Dogs	2	56	One died in convulsions in 4 hours following first exposure. The other dog developed only transitory effects.
Rats	16	153	Loss of weight. Eye, nose irritation. Five death ; survivors poor condition.
	16	100	Weight gain. Slight lethargy, otherwise no toxic effects.
Guinea pigs	16	153	Salivation. Eye, nose irritation. Three death ; survivors fair.
	16	100	Gained weight. Slight lethargy, otherwise no toxic effects.
Rabbits	4	153	Moderate eye and nose irritation. One died.
	3	100	Listless, otherwise normal.
Cats	4	153	In severe distress after each exposure. Marked nasal, eye irritation. One died after second exposure.
	4	100	Loss of weight, vomiting. One died after 11th exposure. Others in good condition.

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Effects on Vegetation

Acrylonitrile vapor concentrations above 8246 mg/m^3 (3800 ppm at STP) were toxic to pea seedlings. Concentrations below the toxic level did not produce any growth irregularities or inhibition.[10]

Other Effects

Acrylonitrile is considered a severe fire and explosion hazard.

AMBIENT CONCENTRATIONS AND MEASUREMENTS

Ambient Concentration Estimates

The largest installation for acrylonitrile production is located in a town of about 11,000 population, and it has a capacity of about 460 million lb/yr. Using the 1 percent emission factor presented in a later section of this report, this converts to an emission rate of:

$$\frac{(0.01 \text{ emission factor})\ (460 \times 10^6 \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}}$$

$$= 66.2 \text{ g/sec of acrylonitrile.}$$

Some assumptions must be made regarding this acrylonitrile release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where acrylonitrile vapor leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[11] To do this a virtual point source of emission is

assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100m/4.3 = 23.3m$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{66.2}{(2)\pi(36)(18.5)} e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 1.366 \times 10^{-2} \text{ g/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes $(1.366 \times 10^{-2} \text{ g/m}^3)(0.72) = 0.984 \times 10^{-2} \text{ g/m}^3$ or 4.6 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 2.6 ppm.

Acrylonitrile Measurement Techniques

Two analytical methods for measuring acrylonitrile in air are the potassium permanganate method[12] and the sulfuric acid method.[13] The first method is sensitive to approximately 10 ppm and the second method is sensitive to approximately 0.5 ppm. Descriptions of the techniques are given below.

In the potassium permanganate method the air sample is drawn through a midget impinger and is bubbled into a solution of potassium permanganate, sodium hydroxide and telluric acid. Approximately 200 ml of air is pulled through the impinger until the permanganate changes color from pink to bluish-green. The concentration is then determined from a calibration curve showing air volume versus parts per million.

Interferences may result from compounds containing double-bonded carbon atoms. This method may not be suitable for air pollution work but is satisfactory for industrial hygiene field work. This procedure requires about 30 minutes for completion.

The sulfuric acid method involves drawing the air sample into an absorber containing sulfuric acid and glass beads. Usually two absorbers in series are used to increase the collection efficiency. After the sample is collected in the absorber, it is refluxed with copper acetate. The sample is then made alkaline with sodium hydroxide and oxidized with hydrogen peroxide while refluxing gently. After 30 minutes the sample is distilled and titrated with sodium hydroxide. The concentration of acrylonitrile is then calculated.

The sampling rate for this method should not exceed 0.4 liters per minute, and approximately 6 mg of acrylonitrile should be collected for an accurate determination. Interferences will result from many nitrogen-containing compounds. This method requires about 2 hours for completion and is suitable for air pollution work.

SOURCES OF ACRYLONITRILE EMISSIONS

Acrylonitrile Production and Consumption

The production of acrylonitrile in 1974 was almost 1,400 million pounds,[14] and it is expected to increase at 9.9 percent per year through 1978. If plastic bottles made from acrylonitrile are readily accepted by the consumer, the expected growth rate could be appreciably higher. Acrylonitrile is primarily used in the production of acrylic fibers for apparel, carpets, blankets, etc., accounting for 57 percent of total production. The second largest use for acrylonitrile is in the production of acrylonitrile-butadiene-styrene (ABS) resins and styrene-acrylonitrile (SAN) resins. The major markets for ABS resins are pipe and pipe fittings, automotive components, refrigerator door linings, and housings for business machines. SAN resins are used primarily in housewares items, automotive instrument panels and instrument leases. Four companies at five locations are currently manufacturing acrylonitrile. See Appendix A for names and locations. The consumption of acrylonitrile for final products is shown in Table 5. This table also presents the expected growth rates for each sector of the market.

Table 5. ESTIMATED ACRYLONITRILE CONSUMPTION - 1974[15]

	Million pounds	% annual growth
Acrylic fibers	791	7.5
ABS resins	240	15.5
SAN resins	28	11.0
Nitrile elastomers	66	3.5
Exports	110	1.0
Adiponitrile	80	20.0
Acrylamide	27	8.5
Miscellaneous	57	27.0
Total	1399	9.9

Acrylonitrile Sources and Emission Estimates

Primary sources of emissions of acrylonitrile occur from acrylonitrile production, end product manufacture, and bulk storage. Total emissions from these categories are estimated to be 31.1 million pounds, representing 2.2 percent of total production. The breakdown by source is given in Table 6.

Table 6. SOURCES AND EMISSION ESTIMATES OF ACRYLONITRILE - 1974

Source	Million pounds/year
Acrylonitrile production	14.1
End product manufacture	13.0
Bulk storage	4.0
Total	31.1

Although a number of chemical routes are available to produce acrylonitrile, only one, ammoxidation of propylene, accounts for all of the acrylonitrile now produced in the United States. The Sohio process uses refinery propylene, fertilizer grade ammonia, and air in the fluidized-bed catalytic reactor. The reaction is presented below.

$$2CH_2 = CH\text{-}CH_3 + 2NH_3 + 3O_2 \longrightarrow 2CH_2 = CH\text{-}CN + 6H_2O$$

propylene ammonia oxygen acrylonitrile

In 1967 a catalyst (trade name Catalyst 21), based on depleted uranium, was used which increased the rate of conversion and produced fewer by-products. In 1972 another catalyst (trade name Catalyst 41), which is uranium free, was introduced and is reported to have increased the yield of acrylonitrile while decreasing emissions. In a recent study concerning acrylonitrile manufacture it is reported that emissions of acrylonitrile from manufacturing processes are approximately 248 pounds per hour

based on a 200 million pound per year plant, or 0.0101 pounds emitted per pound produced.[16] Using this factor and the current production figure (1399 million pounds), emissions of acrylonitrile are 14.1 million pounds per year.

In order to estimate emissions from end product manufacture it is assumed that the same emission factor is applicable. End product consumption of acrylonitrile is approximately 1288 million pounds, resulting in 13.0 million pounds of acrylonitrile emitted.

Because of the moderate vapor pressure of acrylonitrile, storage tanks are considered to be fixed roof tanks and are vented directly to the atmosphere.[16] Emissions estimates based upon factors found in AP-42[17] are 4 million pounds per year.

ACRYLONITRILE EMISSION CONTROL METHODS

Emissions from the manufacture of acrylonitrile occur mainly from the main process vent absorber. Presently, most of the U.S. plants do not have any significant emission control facilities on the absorber vent stream. All plants, however, do use a mist eliminator at the top of the absorber to prevent liquid carryover to the atmosphere. Unfortunately this inexpensive device does not reduce hydrocarbon emissions.

The most practical method of reducing hydrocarbon emissions (and acrylonitrile emissions) in the absorber vent gas is by using one of the following methods, none of which is currently in use at acrylonitrile plants.

1. CO-boiler
2. Thermal incinerator
3. Incinerator plus steam generation
4. Flare system

Cost data presented in the following tables indicate that employing dual CO boilers is not an economical method of reducing emissions. However, if a stand-by boiler is not necessary, this type of control device is about as economical to operate as other combustion devices.

It has been reported[16] that the best control system for new acrylonitrile plants would include a thermal incinerator with a waste heat boiler on the absorber vent. The most feasible method of reducing air emissions from existing plants would be the addition of a thermal incinerator. Cost data for the four control systems are provided in Tables 7, 8, 9 and 10.

Control of emissions from storage tanks requires the use of floating-roof tanks or the venting of emissions to the previously mentioned control equipment. If these systems are not available, fixed roof tanks can be switched to floating roof tanks resulting in a 69 percent reduction of emissions. Figure 1 provides estimated costs of various gasoline storage tanks.[18] These equipment cost estimates can also be applied to acrylonitrile. As can be seen, conversion of fixed roof tanks to floating roof tanks by installation of internal floating covers is more economical than the installation of new pontoon floating tanks.

Table 7. CO-BOILER[a,16]

Number of units required	2
Total flow	440,742 lb/hr 100,550 scfm
Purchased cost	$1,000,000
Installation	$1,500,000
Total capital	$2,500,000
Operating cost[b]	$1,237,000
Steam production (credit)[c]	(785,000)
Total annual cost	$ 452,000
Efficiency	98%

[a]Costs updated to first quarter 1975.

[b]Includes depreciation, interest, maintenance, labor and utilities.

[c]75¢/1000 lbs (450 psig 750°F).

Table 8. THERMAL INCINERATOR[a,16]

Total flow	304,444 lb/hr 69,440 scfm
Purchased cost	$222,000
Installation	$222,000
Total capital	$444,000
Operating cost[b]	$173,000
Total annual cost	$173,000
Efficiency	98%

[a]Costs updated to first quarter 1975.

[b]Includes depreciation, interest, maintenance, labor and utilities.

Table 9. THERMAL INCINERATOR AND WASTE HEAT BOILER[a,16]

Total flow	304,444 lb/hr 69,440 scfm
Purchased cost	$432,000
Installation	$534,000
Total capital	$966,000
Operating cost[b]	$300,000
Steam production (credit)[c]	$152,000
Total annual cost	$148,000
Efficiency	98%

[a]Costs updated to first quarter 1975.

[b]Includes depreciation, interest, maintenance labor and utilities.

[c]75¢/1000 lb (450 psig 750°F).

Table 10. FLARE SYSTEM[a,16]

Total flow	60,000 lb/hr
Total capital cost	$190,000
Operating cost[b]	$787,000
Total annual cost	$787,000
Efficiency	89%

[a]Costs updated to first quarter 1975.

[b]Includes depreciation, interest, maintenance, labor and utilities.

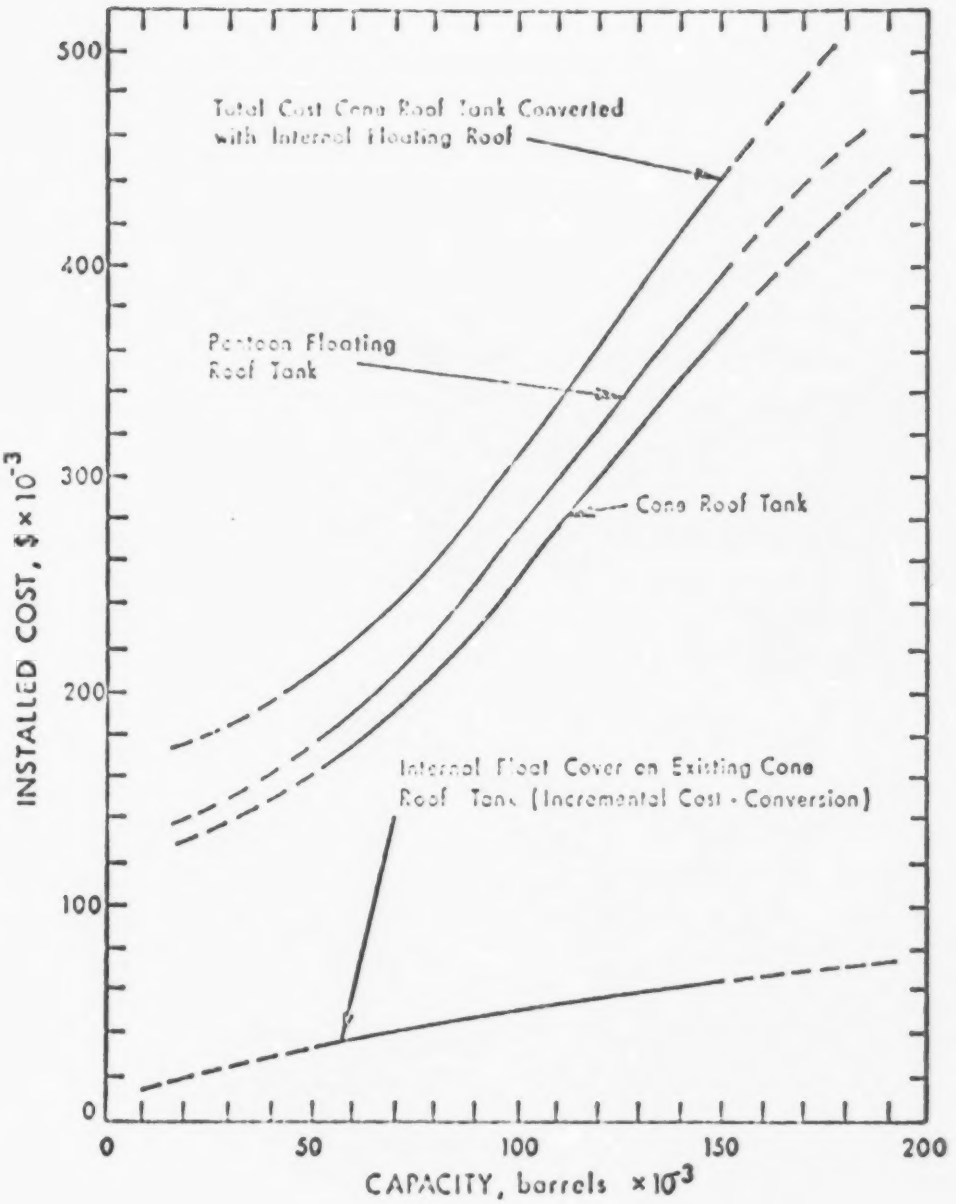

Figure 1. Estimated installed costs of acrylonitrile storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[18]

SECTION III

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APPENDIX A

ACRYLONITRILE MANUFACTURERS[15]

		Capacity, million pounds
American Cyanamid	New Orleans, Louisiana	200
Dupont	Beaumont, Texas	300
Dupont	Memphis, Tennessee	250
Monsanto	Chocolate Bayou, Texas	460
Vistron Corp.	Lima, Ohio	390
	Total	1,600